

IX. APPENDIX II

ANALYTICAL METHOD FOR ISOPROPYL ALCOHOL

Principle of the Method

(a) A known volume of workplace air is drawn through a charcoal tube to trap the isopropyl alcohol.

(b) The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide containing 1% 2-butanol.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

(d) The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

Range and Sensitivity

(a) This method has been validated over the range of 505-1,890 mg/cu m (206-769 ppm) in a test-atmosphere at a temperature of 25 C and pressure of 747 mmHg, using a 3.0-liter air sample. [87] With a sample size of 3.0 liters, the probable range of this method is 100-2,500 mg/cu m (approximately 40-1,000 ppm) at detector sensitivity that gives nearly full deflection on a strip chart recorder for a 6.0-mg aliquot. The method is capable of measuring much smaller amounts, such as 10 ppm, if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

(b) The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the

concentrations of isopropyl alcohol and other substances in the air.

Interferences

(a) When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the amount of organic vapor which can be collected before breakthrough of the primary adsorbing section occurs. Therefore, in case of high humidity, a low volume of air must be sampled. The capacity of the charcoal tube for adsorption of isopropyl alcohol may also be reduced by the presence of another organic vapor in high concentration.

(b) Any compound which has about the same retention time as that of isopropyl alcohol at the gas chromatographic conditions described in this method will interfere with the analysis. This type of interference can be overcome by changing the operating conditions of the instrument, usually the column and/or the column temperature.

Precision and Accuracy

(a) The precision and accuracy values for the analysis of isopropyl alcohol vary from one laboratory to another and from one set of equipment to another.

(b) A desorption efficiency of 96.7% from 1 lot of coconut shell charcoal has been reported. If any other type of charcoal is used, the desorption efficiency must be determined.

Apparatus

- (a) Gas chromatograph equipped with a flame ionization detector.
- (b) Column (10 ft x 1/8 inch) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns such as K-20M carbowax capable of performing the required separations may be used.
- (c) A mechanical or electronic integrator or a recorder and some other method for determining the peak area.
- (d) Glass glass-stoppered test tubes or the equivalent.
- (e) Microsyringes: 10 μ l and other convenient sizes for making standards.
- (f) Volumetric flasks: convenient sizes for making standards.
- (g) Pipets.

Reagents

- (a) Carbon disulfide, containing 1% 2-butanol, reagent grade.
- (b) Isopropyl alcohol.
- (c) Internal standard n-Undecane (99+%) or other suitable standard.
- (d) Purified nitrogen.
- (e) Purified hydrogen.
- (f) Filtered compressed air.

Analytical Procedure

(a) Cleaning of equipment

All glassware used for laboratory analysis should be washed in detergent followed by tap and distilled water rinses.

(b) Analysis of samples

(1) Preparation of samples: Each charcoal tube, including the blank from field samples, is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These 2 sections are analyzed separately.

(2) Desorption of samples: Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each test tube to desorb the isopropyl alcohol from the charcoal. For the internal standard method, a 0.5% solution of internal standard in carbon disulfide is used.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISULFIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that any apparent change in volume during the desorption process can be observed.

(3) Gas chromatographic conditions: The typical operating conditions for the gas chromatograph are:

- (A) 30 cc/min (80 psig) nitrogen carrier gas flow.
- (B) 30 cc/min (50 psig) hydrogen gas flow to detector.
- (C) 300 cc/min (50 psig) airflow detector.
- (D) 200 C injector temperature.
- (E) 300 C manifold temperature (detector).
- (F) 70 C column temperature.
- (G) Isothermal oven, unless temperature programming is necessary to separate interfering substances.

(4) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. The solvent flush injection technique is employed. This eliminates difficulties arising from blowback or distillation within the syringe needle, thus increasing the accuracy and reproducibility of the injected sample volume. The 10.0 μ l-syringe is first flushed with solvent several times to wet the barrel and plunger, then 3.0 μ l of solvent are drawn into the syringe. Next, the needle is removed from the solvent and the plunger is pulled back about 0.2 μ l to separate the solvent flush from the sample with an air pocket to be used as a marker. The needle is then immersed in the sample and a 5.0- μ l aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection in the gas chromatograph, the plunger is pulled back a short distance to minimize sample evaporation from the needle tip. Duplicate injections should be made of each sample and of the standard. No more than a 3% difference should result in the peak areas that are recorded.

Calibration and Standards

It is convenient to express the concentration of the standards in terms of mg/ml of eluent. A series of standards of various concentrations over the range of interest is prepared and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Standard curves are established by plotting concentration in mg/ml carbon disulfide versus the ratio of peak area of isopropyl alcohol to peak area of the internal standard.

Determination of Adsorption and Desorption Efficiencies

This section describes a method for determining adsorption and desorption efficiencies. It must be kept in mind that the desorption efficiency is a function of the amount of isopropyl alcohol for each sample, and that it is not constant for isopropyl alcohol. Hence, if possible, the measured concentration of isopropyl alcohol used should be similar to the concentration expected in the test situation. Unused charcoal tubes from the same batch as that used in obtaining samples in the work area are to be used in this determination. A measured volume of isopropyl alcohol is injected into a bag containing a known volume of air. The bag, made of a material that will not absorb the alcohol, should have a gas sampling valve and a septum injection port. The concentration of isopropyl alcohol in the bag may be calculated, if the temperature and pressure in the bag are known. A measured volume is then drawn through a charcoal tube. At least 5 tubes are prepared in this manner. Desorption and analysis are done in the same manner as the sample. Samples taken with

a syringe from the bag are also injected into the gas chromatograph to confirm the actual concentration in the bag.

$$\frac{\text{Quantity of isopropyl alcohol desorbed from charcoal}}{\text{concentration of isopropyl alcohol in bag}} \times \frac{100}{\text{volume of air drawn through tube}} = \% \text{ Efficiency}$$

Calculations

(a) The weight in mg of isopropyl alcohol, corresponding to each peak area, is read from the standard curve. No volume corrections are needed, because the standard curve is also based on a mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

(b) Corrections for the blank must be made for each sample. The weight of isopropyl alcohol determined for the front section of the blank tube is subtracted from the weight determined for the front section of the sample tube. A similar procedure is followed for the back section.

(c) The corrected amounts present in the front and back sections of the same sample tube are added to determine the total measured amount in the sample.

(d) This total weight is divided by the determined desorption efficiency to obtain the total weight of isopropyl alcohol in mg that was present in the air volume sampled.

(e) Milligrams/cubic meter are converted into parts per million by volume of isopropyl alcohol in the air sampled assuming isopropyl alcohol is an ideal gas, using the following equation:

$$\text{number of parts/million} = \frac{\text{number of mg}}{\text{cu m}} \times \frac{24,450}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{\text{T} + 273}{298}$$

where:

P = pressure (mmHg) of air sampled

T = temperature (C) of air sampled

MW = molecular weight (g/mole) of isopropyl alcohol

24,450 = molar volume (ml/mole) at 25 C and 760 mmHg

760 = standard pressure (mmHg)

298 = standard temperature (K)

X. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "6.8 ml/kg LD50-oral-rat," "16.4 ml/kg LD50-skin-rabbit," or "permissible exposure from 29 CFR 1910.93," or if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flammable or reactive data could be flash point,

shock sensitivity, or other brief data indicating nature of the hazard.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to isopropyl alcohol. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE 1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA				
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
V HEALTH HAZARD INFORMATION				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN:				
INHALATION:				
INGESTION:				
NOTES TO PHYSICIAN				

VI REACTIVITY DATA	
CONDITIONS CONTRIBUTING TO INSTABILITY	
INCOMPATIBILITY	
HAZARDOUS DECOMPOSITION PRODUCTS	
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION	
VII SPILL OR LEAK PROCEDURES	
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	
NEUTRALIZING CHEMICALS	
WASTE DISPOSAL METHOD	
VIII SPECIAL PROTECTION INFORMATION	
VENTILATION REQUIREMENTS	
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT	
RESPIRATORY (SPECIFY IN DETAIL)	
EYE	
GLOVES	
OTHER CLOTHING AND EQUIPMENT	

IX SPECIAL PRECAUTIONS

**PRECAUTIONARY
STATEMENTS**

**OTHER HANDLING AND
STORAGE REQUIREMENTS**

PREPARED BY _____

ADDRESS _____

DATE _____

XI. APPENDIX IV

OCCUPATIONAL RESEARCH PRIORITIES FOR ISOPROPYL ALCOHOL

(1) Acute Effects of Inhalation of Isopropyl Alcohol in Humans

Additional studies should be performed to elucidate the acute effects of isopropyl alcohol inhalation in humans. These studies should be designed to determine whether isopropyl alcohol produces significant skin and eye irritation, changes in respiratory parameters, and liver pathology at various concentrations. Tolerance to these effects should also be evaluated.

(2) An Epidemiologic Study

Since the first study conducted by Weil et al [39] regarding the old process, no epidemiologic studies have been made to see if a high incidence of paranasal sinus cancers prevails in the new process. The need for an epidemiologic study is urgent. A retrospective cohort study would be an important tool in determining whether the cancer rate has significantly changed in the present isopropyl alcohol manufacturing plants.

(3) Chronic Animal Exposure Studies

Exposure of rodents to several concentrations of isopropyl alcohol up to the maximum tolerated concentration, 8 hours/day, 5 days/week, for 18 months is recommended to investigate the possible carcinogenic action of the alcohol and effects of long term exposure. Two types of studies should

be involved, one a dermal application study and the other inhalation.

(4) Acute Animal Exposure Studies

As stated previously, there are numerous information gaps on biochemical effects of isopropyl alcohol at levels that might be encountered in the workplace environment. In this regard, acute animal experiments using levels up to 800 ppm of isopropyl alcohol are essential.

Accumulation of liver triglycerides has been caused by isopropyl alcohol and this phenomenon has been the basis for inferring that fatty liver is produced. [61,62] In light of these effects, additional data are needed to answer two basic questions:

- (a) Is there a dose-response relationship for these effects?
- (b) Is there any histological evidence for isopropyl alcohol-induced fatty liver?

(5) Effect of Isopropyl Alcohol on Chlorinated Hydrocarbon Toxicity

It has been established that isopropyl alcohol intake in large amounts 16-20 hours prior to inhalation of carbon tetrachloride, can increase the toxicity of carbon tetrachloride. [65-67] Again, further studies of animal exposure by inhalation must be done to answer three basic questions:

- (a) Does inhalation of isopropyl alcohol at low levels (below 800 ppm) followed by inhalation of carbon tetrachloride at low levels (below 10 ppm) augment the toxicity of the latter?

(b) Does isopropyl alcohol potentiate the toxicity of other chlorinated hydrocarbons as well?

(c) Is isopropyl alcohol, or acetone, or any other metabolite, the potentiator of carbon tetrachloride toxicity in vivo?

XII. TABLES AND FIGURE

TABLE XII-1

PROPERTIES OF ISOPROPYL ALCOHOL

Appearance	Colorless
Odor	Acrid
Molecular formula	CH ₃ CHOHCH ₃
Formula weight	60.09 g
Boiling point	82.3 C
Freezing point	-89.5 C
Specific gravity	0.7861 at 20 C
Solubility	Miscible with water, ethyl alcohol, and ethyl ether
Flash point	12 C (closed cup)
Ignition temperature	399 C
Lower explosive limit	2%
Relative vapor density	2.07 (air = 1.00)
Vapor pressure	44 mmHg at 25 C 59.1 mmHg at 30 C 105.6 mmHg at 40 C 176.8 mmHg at 50 C
Conversion factors at standard temperature and pressure	1 ppm = 2.46 mg/cu m 1 mg/liter = 407 ppm

Derived from references [1] and [2]

TABLE XII-2
EFFECTS OF ISOPROPYL ALCOHOL IN ANIMALS*

Species	Route of Exposure	Dose	Effects	Reference
Rats	Inhalation	16,000 ppm	Death of 4 of 6 after a single 8-hour exposure	45
"	"	8.13 ppm	Continuous exposure: increased BSP retention, leukocyte counts, abnormal fluorescent leukocytes, changed latent period of unconditional reaction, statistically significant	47
"	"	1.02 ppm	Continuous exposure: same as effects as at 8.13 ppm, not statistically significant	47
"	"	0.24 ppm	Continuous exposure: no effect.	47
Rabbits	Oral	6.5-8.0 ml/kg	Death of 34 of 36 within 80 hours	50
Rats	"	6 g/kg (7.63 ml/kg)	Accumulation of liver triglycerides	61, 62
Rats, Older adult	"	6.8 ml/kg	LD50	52
Rats, Young adult	"	6.0 ml/kg	"	52

TABLE XII-2 (CONTINUED)
EFFECTS OF ISOPROPYL ALCOHOL IN ANIMALS*

Species	Route of Exposure	Dose	Effects	Reference
Rats, 14-day-old	Oral	5.6 ml/kg	LD50	52
Rats	"	3.0 g/kg (3.82 ml/kg)	Accumulation of liver triglycerides	63
"	"	2.58 g/kg (3.28 ml/kg)	Narcosis	51
"	"	2.34 g/kg (2.98 ml/kg)	16-18 hours after alcohol administration, inhalation of CCl ₄ at 1,000 ppm for 2 hours resulted in increased SGOT level.	65
Rabbits	"	2.5 ml/kg	Narcosis	50
Mice	"	"	Single doses (0.05-2.5 ml/kg) of 4 chlorinated hydrocarbons were administered 18 hours after alcohol: augmented hepatotoxicity of 3 hydrocarbons.	68
Rabbits	Dermal	16.4 ml/kg	LD50	45

*Results of additional cancer studies on animals are included in Chapter III

FIGURE XII-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH CHARCOAL TUBE



